CHEMISTRY LETTERS, pp. 1303-1306, 1990.

Novel Disilylation and Germylation of Coordinated Dinitrogen in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$[1]

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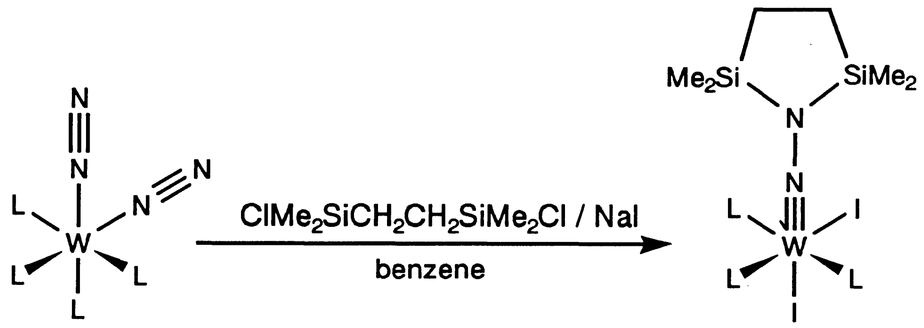
When treated with a mixture of $ClMe_2SiCH_2CH_2SiMe_2Cl$ and excess NaI, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$(1) afforded *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$, the structure of which was determined by the X-ray analysis. On the other hand, treatment of 1 with Me_3GeCl in the presence of excess NaI gave two germylated dinitrogen complexes *trans*-$[WI(NNGeMe_3)(PMe_2Ph)_4]$ and *mer*-$[WI_2(NNHGeMe_3)(PMe_2Ph)_3]$.

We previously reported that a series of Mo and W dinitrogen complexes $M(N_2)_2(L)_4$ (M = Mo, W; L = PMe_2Ph, 1/2dpe; dpe = $Ph_2PCH_2CH_2PPh_2$) react with Me_3SiX (X = I, CF_3SO_3) to give the silyldiazenido complexes *trans*-$[MX(NNSiMe_3)(L)_4]$ and the silylhydrazido(2-) complexes *mer*-$[MX_2(NNHSiMe_3)(PMe_2Ph)_3]$ or $[MX(NNHSiMe_3)(dpe)_2]X$.[2,3] Following this discovery, we have recently found the reaction system in which N_2 gas is catalytically converted into silylamines such as $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ in the presence of these dinitrogen complexes.[4] In this paper, we wish to report the novel disilylation and germylation of the coordinated dinitrogen in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$(1) using the systems, $ClMe_2SiCH_2CH_2SiMe_2Cl$/NaI and Me_3GeCl/NaI, respectively.

Treatment of complex 1 with $ClMe_2SiCH_2CH_2SiMe_2Cl$ in the presence of excess NaI at 50 °C in benzene for 45 h in the dark gave a disilylhydrazido(2-) complex *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$(2),[5] which was isolated as brown crystals in 49% yield by the addition of hexane to the product solution (Eq. 1). It is to be noted that no disilylated complexes were obtained by the reactions of the



1 (L = PMe_2Ph) 2 (1)

dinitrogen complexes with Me$_3$SiX (X= I, CF$_3$SO$_3$).[2,3] The structure of complex **2** determined by the X-ray analysis is depicted in Fig. 1.[6] A W-N-N linkage is essentially linear (174.3(7)°) and the two carbon, two silicon and one nitrogen atoms consisting of a five membered ring together with the inner nitrogen and tungsten atoms lie almost on the same plane. The Si-N bond distances are 1.79(1) and 1.78(1) Å, the W-N and N-N bond lengths being 1.76(8) and 1.36(1) Å, respectively. These bond lengths and angles well correspond to those of silylhydrazido(2-) complex *mer*-[WI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$](**3**) reported previously.[2] Since no silylated complexes were produced in the absence of NaI, the formation of complex **2** presumably takes place by the electrophilic attack of IMe$_2$SiCH$_2$CH$_2$SiMe$_2$I generated *in situ*[7] on the terminal nitrogen atom.

Analogous treatment of complex **1** with Me$_3$GeCl/NaI for 70 h at 50 °C gave orange crystals of *trans*-[WI(NNGeMe$_3$)(PMe$_2$Ph)$_4$](**4**)[8] in 23% yield. In the IR spectrum of this complex appears a strong band characteristic of ν(N=N) at 1530 cm^{-1}, whereas the ^{1}H NMR spectrum shows two singlets at 0.36 and 1.74 ppm assignable to Ge-CH$_3$ and P-CH$_3$ protons. As summarized in Table 1, these spectroscopic data well correspond to those observed for *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] that has been fully characterized by the X-ray crystallography.[2] In addition to complex **4**, brown crystals were also isolated from the reaction mixture in a low yield. The elemental analysis, IR, and ^{1}H NMR data are diagnostic of the formation of this product as *mer*-[WI$_2$(NNHGeMe$_3$)(PMe$_2$Ph)$_3$](**5**) (Eq. 2),[9] if compared with those of complex **3**

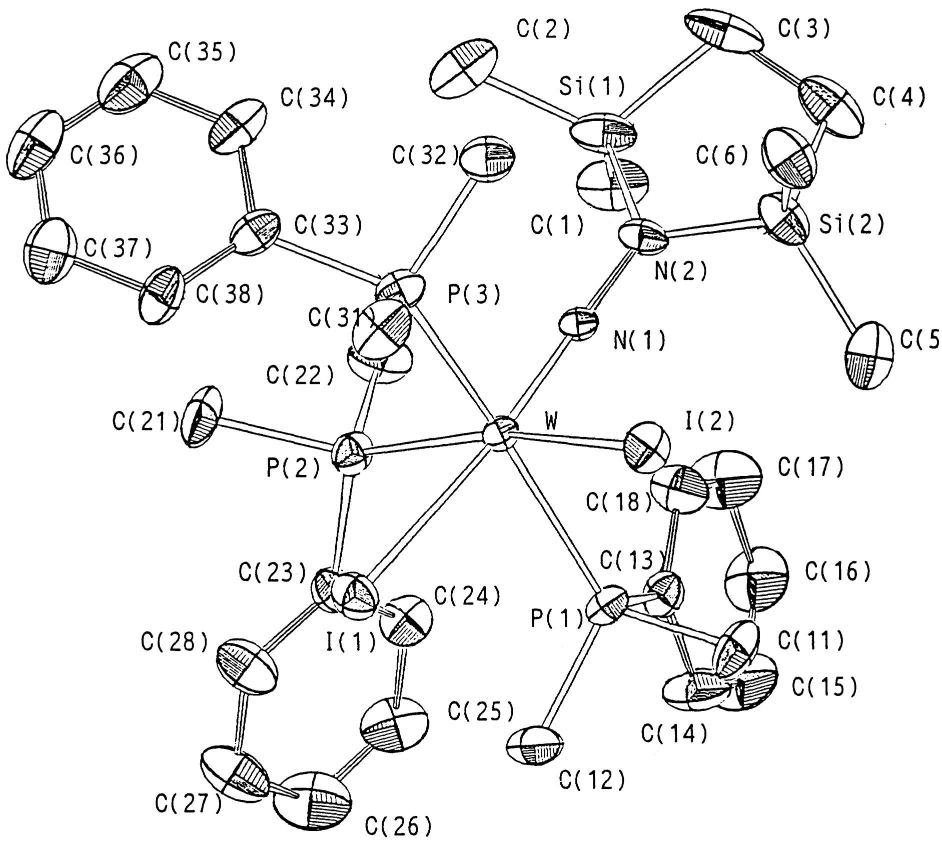
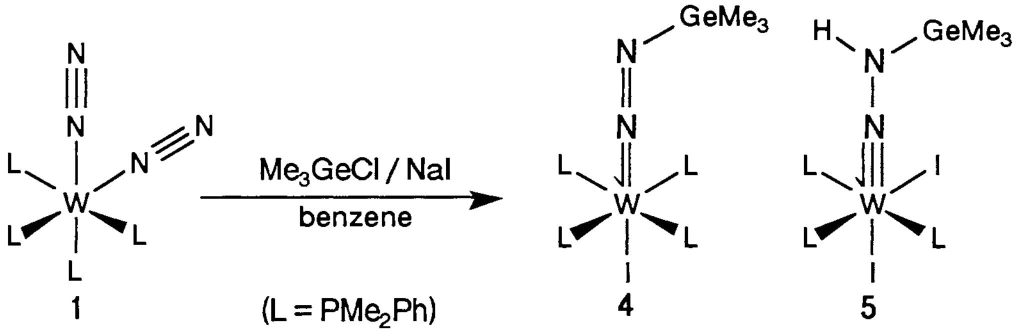


Fig. 1. An ORTEP drawing of molecule *mer*-[WI$_2$(N$\overline{\text{NSiMe}_2\text{CH}_2\text{CH}_2\text{Si}}Me_2$)(PMe$_2$Ph)$_3$](**2**).

(Table 1).[10] Trials to determine the detailed structures of these novel germylated dinitrogen complexes by the X-ray analyses were not successful because of the extreme instability of these compounds under the conditions of the X-ray data collection.



(2)

Complexes **4** and **5** are the first examples of the Ge-N bond formation of coordinated dinitrogen, although several examples of alkylated[11] and silylated[2,3] dinitrogen complexes have already been reported. These two trimethylgermylated dinitrogen complexes are less stable, especially in solution, than the corresponding trimethylsilylated dinitrogen complexes. Further investigations on the silylation and germylation of coordinated dinitrogen are in progress.

The financial support by the Ministry of Education of Japan and the Asahi Glass Foundation for Industrial Technology is greatly appreciated.

Table 1. Comparison of IR and ^1H NMR Data for Germylated Dinitrogen Complexes with Those for Silyl Analogues

Complex	IR[a]		^1H NMR[b]		
	ν(NN)	ν(NH)	Si-C$\underline{H}_3$ or Ge-C$\underline{H}_3$	P-C$\underline{H}_3$	N-$\underline{H}$
Diazenido complexes					
trans-$[WI(NNGeMe_3)(PMe_2Ph)_4]$(4)[c]	1530	-	0.36(s, 9H)	1.74(s, 24H)	-
trans-$[WI(NNSiMe_3)(PMe_2Ph)_4]$[d]	1580	-	0.42(s, 9H)	1.68(s, 24H)	-
Hydrazido(2-) complexes					
mer-$[WI_2(NNHGeMe_3)(PMe_2Ph)_3]$(5)[c]	1351	3260	0.20(s, 9H)	1.55(d, 6H) 2.30(t, 6H) 2.36(t, 6H)	2.88(s, 1H)
mer-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$(3)[d]	1360	3250	-0.07(s, 9H)	1.41(d, 6H) 2.24(2t, 12H)	2.08(s, 1H)

a) cm^{-1}; KBr disks. b) δ; C_6D_6 solution: referred to C_6D_5H in C_6D_6 at 7.20 ppm; phenyl protons are omitted. c) This work. d) Ref. 2.

References

1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes 28. Part 27: T. Ishida, Y. Mizobe, and M. Hidai, *Chem. Lett*, **1989**, 2077.

2) M. Hidai, K. Komori, T. Kodama, D.-M. Jin, T. Takahashi, S. Sugiura, Y. Uchida, and Y. Mizobe, *J. Organomet. Chem.*, **272**, 155 (1984).

3) K. Komori, S. Sugiura, Y. Mizobe, M. Yamada, and M. Hidai, *Bull. Chem. Soc. Jpn.*, **62**, 2953 (1989).

4) K. Komori, H. Oshita, Y. Mizobe, and M. Hidai, *J. Am. Chem. Soc.*, **111**, 1939 (1989).

5) *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$: Found: C, 34.02; H, 4.63; N, 2.69%. Calcd for $C_{30}H_{49}N_2I_2P_3Si_2W$: C, 35.17; H, 4.82; N, 2.73%. IR (KBr disk, cm^{-1}) ν(NN), 1311s; ν(SiN), 855m. ^1H NMR (C_6D_6 solution, ppm) 0.47 (s, 12H, $SiMe_3$); 0.59 (s, 4H, $SiCH_2$); 1.52 (d, 6H, PMe); 2.17 (t, 6H, PMe); 2.20 (t, 6H, PMe); 6.7 - 7.8 (m, 15H, PPh).

6) Crystal data for complex **2**: M = 1024.5, monoclinic, space group $P2_1/n$, a = 14.378(4), b = 25.657(4), c = 10.601(2) Å, β = 95.58(2)°, U = 3891.9(14) $Å^3$, Z = 4, D_{calcd} = 1.748 g $\cdot cm^{-3}$, μ(Mo Kα) = 48.06 cm^{-1}, R = 0.065, Rw = 0.068 for 7760 reflections ($|Fo| > 3\sigma(|Fo|)$).

7) The mixture of Me_3SiCl and NaI can be used as a convenient and inexpensive alternative for Me_3SiI. For example, see: T. Morita, Y. Okamoto, and H. Sakurai, *Yuki Gosei Kagaku Kyokai Shi*, **39**, 973 (1981) and references cited therein.

8) *trans*-$[WI(NNGeMe_3)(PMe_2Ph)_4]$: Found: C, 40.88; H, 5.18; N, 2.53%. Calcd for $C_{35}H_{53}N_2GeIP_4W$: C, 41.66; H, 5.29; N, 2.78%.

9) *mer*-$[WI_2(NNHGeMe_3)(PMe_2Ph)_3]$: Found: C, 33.40; H, 4.37; N, 2.85%. Calcd for $C_{27}H_{43}N_2GeI_2P_3W$; C, 32.47; H, 4.34; N, 2.80%.

10) Since only complex **4** can be obtained in moderate yield under extremely dry conditions, complex **5** presumably results from the further reaction of complex **4** with HI, which is generated *in situ* by the reaction of Me_3GeI and adventitious moisture.

11) For example, see: M. Hidai and Y. Mizobe, "Reactions of Coordinated Ligands," ed by P. S. Braterman, Plenum Press (1989), Vol. 2, p. 53.

(Received May 15, 1990)